

Topic 13: Chemical Equilibria

Knowledge of the concepts introduced in Unit 2, Topic 9B Chemical Equilibria will be assumed and extended in this topic.

Students will be assessed on their ability to:

13.1	be able to deduce an expression for K_c , for homogeneous and heterogeneous systems, in terms of equilibrium concentrations
Square brackets [] indicate conc. in mol/dm ³ so do not use those in K_p . Unit of K_c varies depending on equation	A homogenous reaction is a reaction in which all reactants and products are in the same phase A heterogeneous reaction is a reaction in which at least one of the reactants and/or products is in a different phase to the others All reversible reactions reach dynamic equilibrium Recall that dynamic equilibrium is reached when the <i>rate of forward reaction equals rate of backward reaction</i> , the reaction is continuous and <i>concentrations of reactants and products are constant</i> Equilibrium constant is the number that links the equilibrium constant, K , to the concentrations of reactants and products at equilibrium taking the stoichiometry of the equation into account (at a given temperature) For a given reaction: $aA + bB \rightleftharpoons cC + dD$ Solids are ignored in both K_c and K_p K_c of a reaction only changes with <i>changes in temperature</i>
13.2	be able to deduce an expression for K_p for homogeneous and heterogeneous systems, in terms of equilibrium partial pressures in atm
Unit of K_p varies depending on equation	If a reaction contains gases, an alternative equilibrium expression can be set up using the partial pressures of the gases instead of concentrations- this is called K_p The partial pressure of a gas in a mixture is the pressure that the gas would have if it alone occupied the whole volume of mixture Total pressure = sum of all partial pressures, $p = p_1 + p_2 + p_3$ Partial pressure = Mole fraction of gas x Total pressure of gas Mole fraction = number of moles / total number of moles of gas
13.3	be able to calculate a value, with units where appropriate, for the equilibrium constants (K_c and K_p) for homogeneous and heterogeneous reactions, from experimental data
13.4	understand how, if at all, a change in temperature, pressure or the presence of a catalyst affects the equilibrium composition in a homogeneous or heterogeneous system
K_c and K_p only change with temperature	<u>Effect of Temperature</u> on equilibrium composition Previously, we have learned that an increase in temperature will shift the position of equilibrium in the endothermic direction and a decrease in temperature will shift it in the exothermic direction to reverse the change Consider a reaction with a forward exothermic reaction, an increase in temperature will shift the position of equilibrium to the left This causes a decrease in K_c as the ratio of [products] to [reactants] decreases The opposite is true for a forward endothermic reaction, an increase in temperature will cause an increase in K_c The same is also true for K_p <u>Effect of Pressure</u> Previously, we have learned that an increase in pressure will shift the position of equilibrium to the side with fewer moles of gas and a decrease in pressure will shift it to the side with more moles of gas Changes in pressure only affect reactions where reactants and products are gases

	<p>Value of K_c is not affected (as this does not involve gases)</p> <p>Value of K_p is not affected (as any changes in pressure causes a shift in position of equilibrium which restores the value of K_p)</p> <p><u>Effect of a Catalyst</u></p> <p>It has no effect on K_c or K_p as a catalyst increases the rate of both forward and backward reactions by the same amount</p> <p>It only speeds up the rate at which equilibrium is established</p>									
13.5	understand that the value of the equilibrium constant is not affected by changes in concentration or pressure or by the addition of a catalyst									
	<p><u>Effect of Concentration</u></p> <p>Previously we have learned that an increase in concentration of reactants shifts the position of equilibrium to the product side and vice versa</p> <p>When the concentration of a reactant or product is changed, there is an immediate change in the reaction quotient (which is the mathematical relationship between concentrations of products and reactants) This makes the reaction quotient not equal to K_c so the position of equilibrium shifts to reverse this change</p> <p>Hence, changes in concentration have no effect on K_c or K_p</p> <div style="border: 1px solid black; padding: 5px;"> <p>So just what is a reaction quotient?!</p> <p>For a general reaction: $aA + bB \rightleftharpoons cC + dD$</p> $Q_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$ <p>At equilibrium, $Q_c = K_c$</p> </div> <p><u>Effect of Pressure</u></p> <p>A change in pressure, at a constant temperature, on an equilibrium system containing gases has no effect</p> <p>Any change in the equilibrium position occurs to maintain the equilibrium constant at a constant value</p> <p><u>Effect of addition of a Catalyst</u></p> <p>It has no effect; it only speeds up the rate at which equilibrium is established</p> <p>This is because it increases the rate of both the forward and backward reaction to the same extent</p>									
13.6	know the effect of changing the temperature on the equilibrium constant (K_c and K_p) for both exothermic and endothermic reactions									
	<p>Effect of Temperature on K_c and K_p</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th>Thermicity of Reaction</th> <th>Increase in temperature</th> <th>Decrease in temperature</th> </tr> </thead> <tbody> <tr> <td>Exothermic</td> <td>K decreases</td> <td>K increases</td> </tr> <tr> <td>Endothermic</td> <td>K increases</td> <td>K decreases</td> </tr> </tbody> </table>	Thermicity of Reaction	Increase in temperature	Decrease in temperature	Exothermic	K decreases	K increases	Endothermic	K increases	K decreases
Thermicity of Reaction	Increase in temperature	Decrease in temperature								
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13.7	understand that the effect of temperature on the position of equilibrium is explained using a change in the value of the equilibrium constant									

13.8	<p>understand the effect of a change in temperature on:</p> <ul style="list-style-type: none"> i the value of ΔS_{total} ii the magnitude of the equilibrium constant, since $\Delta S_{\text{total}} = R \ln K$
i	<p>Recall that $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$</p> <p>$\Delta S_{\text{total}}$ is positive for all spontaneous changes</p> <p>A change in temperature has no or very little effect on ΔS_{system} but a significant effect on $\Delta S_{\text{surroundings}}$</p> $\Delta S_{\text{Sur}}^{\theta} = - \frac{\Delta H}{T}$ <p>We can use this information to predict whether a reaction is spontaneous at a given temperature</p> <p>For a reversible reaction that can reach equilibrium, the equilibrium position can be reached from either side of the reaction</p> <p>This means that both the forward and backward reactions are spontaneous so ΔS_{total} must be positive in both directions</p>
ii	$\Delta S_{\text{total}} = R \ln K$ <p>Hence, we can find out K by rearranging: $K = e^{S_{\text{(total)}}/R}$</p>
13.9	<p>be able to apply knowledge of the value of equilibrium constants to predict the extent to which a reaction takes place</p>
	<p>In general,</p> <p>A large value of K means the equilibrium position is shifted to the product side (RHS)</p> <p>A small value of K means the equilibrium position is shifted to the reactant side (LHS)</p>
	<p>Further suggested practicals:</p> <ul style="list-style-type: none"> i the reaction of ethanol and ethanoic acid (this can be used as an example of the use of ICT to present and analyse data) ii the equilibrium $\text{Fe}^{2+}(\text{aq}) + \text{Ag}^{+}(\text{aq}) \rightleftharpoons \text{Fe}^{3+}(\text{aq}) + \text{Ag}(\text{s})$ iii the distribution of ammonia or iodine between two immiscible solvents iv the thermal decomposition of ammonium chloride v the effect of temperature and pressure changes in the system $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$